Efficient photocatalytic hydrogen evolution over carbon supported antiperovskite cobalt zinc nitride

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Abstract

Photocatalytic solar to chemical energy conversion is an important energy conversion process but suffer from low efficiency. Thus, development of efficient photocatalytic system using earth-abundant elements with low costs is highly desirable. Here, antiperovskite cobalt zinc nitride has been synthesized and coupled with carbon black (Co$_3$ZnN/C) for visible light driven hydrogen production in an Eosin Y-sensitized system. Replacement of cobalt atom by zinc atom leads to an improved charge transfer kinetics and catalytic properties compared with Co$_4$N. Density functional theory (DFT) calculations further reveal the adjusted electronic structure of Co$_3$ZnN by zinc atom introducing. The lower antibonding energy states of Co$_3$ZnN are beneficial for the hydrogen desorption. Moreover, carbon black as support effectively reduces the particle size of Co$_3$ZnN and benefits to the electron storage and adsorption capabilities. The optimal Co$_3$ZnN/C catalysts exhibit the H$_2$ evolution rate of 15.4 μmol mg$^{-1}$ h$^{-1}$, which is over 6 times higher than that of monometallic Co$_4$N. It is even greater than those of most of Eosin Y-sensitized systems.

Keywords: Transition metal nitride; Antiperovskite materials; Particle-size control; Carbon support; Hydrogen evolution;
1. Introduction

Solar to chemical energy conversion is a potential way to meet the urgent demand for renewable and clean energy [1, 2]. So far, noble metal-based materials are generally considered as the best photocatalyst or co-catalyst due to their small over-potential and unique electronic structures [3, 4]. However, limited natural abundance restricts their application on a large scale [5]. In this case, continuative exploitation of efficient and stable alternative non-noble-metal based photocatalytic systems has great significance. Recent developments in transition metal nitrides (TMNs) materials supply a new direction for selecting non-noble-metal based catalysts [6, 7]. Compared to other materials, TMNs have attracted widespread interest due to their high chemical stability and low electrical resistance [8, 9]. The d-bands of the TMNs produce a contraction compared to their parent metals which causes a greater density of states (DOS) near the Fermi level [10]. The redistributions by the DOS in TMNs give them similar properties to group VIII noble metal materials [11]. Therefore, TMNs-based materials have shown their potential for solar to chemical energy conversion in the field of photocatalysis [12, 13].

Recently, cobalt-based nitrides have been reported as multifunctional catalysts for both photocatalytic hydrogen evolution and CO$_2$ reduction due to their unique electronic properties [14]. However, because of the harsh synthetic conditions, monometallic cobalt nitrides generally exhibit large particle size with low surface area and less active sites [15, 16]. Thus, the photocatalytic efficiency of monometallic cobalt nitrides-based catalysts is insufficient. Further optimizations of cobalt-based nitrides in components, structures as well as morphologies are highly desirable to develop novel TMNs-based photocatalyst with superior efficiency. The properties of metallic atoms heavily affect the catalytic properties of TMNs materials [17, 18]. Introducing another metallic atom with suitable atomic radius and electronic properties, forming
bimetallic cobalt-based nitrides is considered to be effective for improving the catalytic efficiency of cobalt nitrides [19].

Here, we report a bimetallic cobalt-zinc nitride (Co$_3$ZnN) coupled with carbon black (Co$_3$ZnN/C) for Eosin Y-sensitized photocatalytic hydrogen evolution under visible light irradiation. Zinc atoms replace the cobalt atoms at the apex of the cubic unit cell forming antiperovskite phase Co$_3$ZnN with improved electronic properties as compared to Co$_4$N. Density functional theory (DFT) calculations reveal the adjusted electronic structure of Co$_3$ZnN by zinc atom introducing. The lower antibonding energy states of Co$_3$ZnN are beneficial for the hydrogen desorption. Moreover, using carbon black as a support, the particle size of Co$_3$ZnN has been effectively reduced to the nanometer scale. It leads to increased adsorption and electronic storage capabilities of Co$_3$ZnN/C. Therefore, Co$_3$ZnN/C exhibits the highest H$_2$ evolution rate of 15.4 μmol mg$^{-1}$ h$^{-1}$, which is over 6 times higher than that of monometallic Co$_4$N. In fact, it is superior as compared with most cobalt-based materials systems and other non-precious metal-based systems.

2. Results and discussion

As illustrated in Scheme S1, a series of transition metal nitrides (TMNs) have been synthesized by nitriding the nitrate precursors (Fig. S1) at 600 °C for 1 h. XRD Rietveld refinement analysis confirms the successful formation of cubic phase Co$_4$N and Co$_3$ZnN without crystalline impurities (Fig. 1a and Fig. 1b). Interestingly, Co$_3$ZnN exhibits an antiperovskite structure which endows it a diverse array of unconventional physical and chemical properties as reported before [20-22]. Since the electronegativity of Zn is smaller than N and Co, the substitution of Co at A-site in Co$_4$N using Zn increased the electron density between B-site N
and X-site Co. Because the electrical conduction in the perovskite-structured compound is mostly contributed by the B-X-B network, the substitution could lead to better conductivity. In fact, Co$_3$ZnN even exhibits lower electrical resistance than commercial carbon black (Fig. S2). It indicates the superior electronic transfer properties of Co$_3$ZnN as compared to that of Co$_4$N. In addition, DFT calculated charge density distribution results further confirm the advantages of Co$_3$ZnN with antiperovskite structure. As shown in Fig. 1c-d, a more negative charge can be observed at N-Co-N network in Co$_3$ZnN than that in Co$_4$N, which contributes better electrical conduction. Co$_3$ZnN/C nanocomposites show similar crystalline phase with Co$_3$ZnN except for additional diffraction peak for carbon black (Fig. S3). According to the computing results of the Debye-Scherrer equation, the size of crystalline grain for Co$_3$ZnN gradually decreases as the carbon content increases. It is consistent with the results of morphology analysis by electron microscopes. As shown in Fig. 2a and Fig. S4, pure Co$_3$ZnN exhibits an irregular bulk morphology with the size around 200-400 nm, which is pretty similar to that of Co$_4$N. The large size is likely inherited from its precursor (Fig. S1), which forms by shrinkage of the larger sized precursor samples. The high-resolution transmission electron microscopy (HRTEM) image reveals two interplanar spacing of 0.265 nm and 0.216 nm in Co$_3$ZnN (Fig. 2b), corresponding to the (110) and (111) plane, respectively. It is in agreement with XRD results. After introducing carbon black as a support, the size of Co$_3$ZnN can be successfully modulated. As shown in Fig. S5 and Fig. 2c, the Co$_3$ZnN/C maintains the morphology and size of the carbon black. The particle size of Co$_3$ZnN in Co$_3$ZnN/C is substantially reduced to 20-30 nm. Besides, the intimate contact between Co$_3$ZnN nanoparticles and carbon black can be found in Fig. 2d, which benefits the electrons transfer capability of Co$_3$ZnN/C.
The compositions and chemical states of the three catalysts are further confirmed by X-ray photoelectron spectroscopy (XPS) and Raman spectra (Fig. 3 and Fig. S6). The high-resolution spectrum of Co 2p in Fig. 3a depicts Co 2p orbitals and two corresponding satellites. The fitted high-resolution Co 2p spectra of the three different catalysts all present three forms of Co species. For the Co4N sample, the dominant peaks at 782.84 eV and 801.60 eV are from Co3+ coordinated to O or N ions, and are attributed to the transition metal nitride phase [19, 23]. The metallic Co0 (Co-Co) can be seen at 778.86 eV and 795.25 eV, and the Co2+ coordinated to O which appears at 780.85 eV and 797.22 eV [24, 25]. The inevitable oxidation on the surface of transitional metal nitride with metallic characteristics leads to such surface states. The ultrathin oxidized layer protects the transition metal nitrides from further oxidation and does not offer any discernible hindrance to fast electron transport [16]. The peaks of Co0 and Co3+ exhibit a negative shift for Co3ZnN compared with Co4N, indicating the tunable electronic structure after the accession of zinc [26]. As carbon black are introduced into the system of Co3ZnN, the peaks of Co0 and Co3+ shift to the higher binding energy. It reveals the charge transfer to the transition metal nitride is taking place [27]. The similar shift trend of Zn 2p binding energies of these two catalysts further confirms this process (Fig. 3b). The N 1s peaks can be deconvoluted into two for Co4N, corresponding to N-Co (397.19 eV) and N-O (399.60 eV), which proves that it is essentially a metal nitride (Fig. 3c) [17, 28]. The new peak at 397.99 eV for Co3ZnN is considered as N-Zn bonds, further confirms this unique bimetallic structure [29]. In the Raman spectrum of Co4N (Fig. 3d), four Raman bands centered at 470, 510 and 607, as well as 675 cm\(^{-1}\) correspond to the E\(_g\), F\(_{2g}\), and A\(_{1g}\) vibration modes of CoO\(_x\), respectively [30]. It is in agreement with the inevitable surface oxidation of TMNs, which has also been confirmed by XPS results. A new Raman peak observed at 692 cm\(^{-1}\) for Co3ZnN has been assigned to the A\(_{1g}\) vibration modes.
of the ZnCo$_2$O$_4$ phase, which further confirms the form of bimetallic structure [31]. After adding carbon black, the Raman peaks have no change suggest the major structures of Co$_3$ZnN are preserved in the composites.

The photocatalytic activities of as-prepared TMNs samples for hydrogen production are estimated in an Eosin Y-sensitized system under visible light irradiation. All the TMNs samples in the absence of Eosin Y are not active under identical conditions (Fig. S7a), indicating that the photoactivity for H$_2$ evolution is driven by electrons from the light excitation of Eosin Y sensitizer. As shown in Fig. 4a, due to the large particle size and less exposed active sites, the H$_2$-generation rate of monometallic nitrides Co$_4$N is only 2 μmol mg$^{-1}$ h$^{-1}$. Bimetallic nitride Co$_3$ZnN exhibits obviously superior catalytic performance (7.2 μmol mg$^{-1}$ h$^{-1}$) as compared to that of Co$_4$N, due to its modulated electronic structure by Zn and excellent electron transfer capability caused by its antiperovskite structure. After optimization by introduction of carbon black as support, a series of Co$_3$ZnN/C samples show better catalytic performance than those of Co$_3$ZnN and Co$_4$N (Fig. S7b). Notably, much loading amount of carbon black would lead to the gradually reduced activity, which could be ascribed to the reduction of reactive sites (Co$_3$ZnN) for hydrogen evolution in the Co$_3$ZnN/C nanocomposites. With further optimizing reaction conditions (Fig. S7c-d), the optimal Co$_3$ZnN/C(1:1) sample shows H$_2$ generation rate of 15.4 μmol mg$^{-1}$ h$^{-1}$, which is superior as compared to most previous reported cobalt-based catalysts (Table S2). In fact, this result is even better than those of most previous reported photocatalytic Eosin Y-sensitized systems with none-noble-metal catalysts (Table S3).

Photo-stability is important to the practical applications of the catalysts. Therefore, the photo-stability of Co$_3$ZnN/C(1:1) has been tested. As shown in Fig. S8a, Co$_3$ZnN/C(1:1) shows that around 28.8 % of activity loss has been found after five cycles of reaction tests. It is due to the
consumption of the TEOA and Eosin Y in the systems (Fig. S8b). After 5 cycles, Co₃ZnN/C(1:1) has been collected and washed by water and ethanol several times. By supplementing the same amounts of the TEOA and Eosin Y, the reclaimed Co₃ZnN/C(1:1) exhibits a similar H₂ evolution rate as compared to that of the first cycle, suggesting the fine stability of Co₃ZnN/C(1:1) (Fig. S9a). In addition, XRD and SEM analysis have also been tested to further confirm the stability of Co₃ZnN/C(1:1). As shown in Fig. S9b, Co₃ZnN/C(1:1) exhibits similar crystal structure before and after reaction. SEM image of reclaimed Co₃ZnN/C(1:1) after reaction displays similar morphology with that of fresh Co₃ZnN/C(1:1) (Fig. S9c). Therefore, it can be concluded that Co₃ZnN/C(1:1) shows excellent photo-stability in Eosin Y-sensitized systems during visible light irradiation.

Owing to the introduction of carbon black, a high specific area for Co₃ZnN/C can be expected. As shown in Table S1 and Fig. S10, Co₃ZnN/C(1:1) exhibits an extremely high surface area (114.20 m² g⁻¹) and pore volume (0.21 cm³ g⁻¹) compared with bulk Co₄N (3.01 m² g⁻¹ and 0.021 cm³ g⁻¹) and Co₃ZnN (3.50 m² g⁻¹ and 0.021 cm³ g⁻¹). The introduction of carbon black increased the specific surface area of the sample by approximately 33 times. Thus, Co₃ZnN/C(1:1) has the best ability to adsorb Eosin Y in three samples (Fig. S11). Moreover, although all the three catalysts show full band absorption, Co₃ZnN/C composite has the strongest optical absorption capacity (Fig. S12). All the advantages of adding carbon black may further promote the photocatalytic activity of Co₃ZnN.

To decipher the original reasons for the promoted photocatalytic activity of bimetallic nitride Co₃ZnN and Co₃ZnN/C nanocomposites, a series of photoluminescence (PL) and electrochemical studies are conducted. Co₃ZnN exhibits a lower PL intensity than Co₄N (Fig. S13), suggesting a more prominent suppression of the recombination of electron and excited
state of Eosin Y [32, 33]. The introduction of carbon black further boosts this suppression effect. The polarization curves reveal an evidently higher current density for Co$_3$ZnN than Co$_4$N (Fig. 4b), indicating improved charge transfer kinetics by the bimetallic structure of Co$_3$ZnN [34]. Co$_3$ZnN/C(1:1) sample displays the highest current density and lowest over-potential, which is attributed to the fact that the spatial distribution of Co$_3$ZnN in the composites enables the exposure of more available active sites on the Co$_3$ZnN surface [35]. Electrochemical impedance spectroscopy (EIS) spectra are shown in Fig. 4c, Co$_3$ZnN exhibits an improved charge transfer compared with the Co$_4$N. Surprisingly, although the electrochemical impedance of pure carbon black is higher than that of the Co$_3$ZnN, the combination of carbon black and Co$_3$ZnN shows the most efficient charge transfer [36]. This further proves the synergistic effect between carbon black and Co$_3$ZnN.

Co$_3$ZnN reveals a larger area enclosed than the Co$_4$N in Fig. S14, which suggests Zinc atoms in the system of antiperovskite can facilitate electronic storage (the inset of Fig. S14). When adding carbon black in the system of Co$_3$ZnN, the specific capacitance of the sample gets a theatrical boost compared with pure Co$_3$ZnN. As such, it is reasonable to claim that the electrons from the photoexcitation of Eosin Y can be further stored by nitrogen-doped carbon black of the composite [37]. Meanwhile, the bimetallic nitride Co$_3$ZnN has a high electrochemical double-layer capacitance ($C_{dl} = 0.054$ mF/cm$^2$) than that of monometallic nitride Co$_4$N ($C_{dl} = 0.038$ mF/cm$^2$), indicating cobalt and zinc bimetallic structure exposes more active sites for reactions than cobalt monometallic structure (Fig. S15) [38]. It also provides another powerful explanation for the excellent performance of bimetallic nitride Co$_3$ZnN. Although the Co$_3$ZnN/C composite shows a more exaggerated capacitance enhanced, combined with the low photocatalytic activity
of carbon black (only 1.7 µmol/h), which indicates that the carbon black is generally as electronic storage stations rather than active sites.

In addition, hydrogen temperature programmed desorption (TPD) of Co4N and Co3ZnN/C have been tested. As shown in Fig. 4d, Co4N exhibits a small H2 desorption peak at about 182 °C and then a broad H2 desorption peak at 340 °C. These results indicate that there exist at least two sites on the Co4N surface for H2 chemisorption: weak and strong chemisorption sites. For Co3ZnN/C, desorption temperatures from both sites evidently decrease to 167 °C and 250 °C, respectively. The decrease in desorption temperatures means that the adsorbed hydrogen species have weaker interactions with Co3ZnN/C surface and thus have a higher reactivity. Moreover, a new sharp peak at 439 °C has also been observed. It suggests a new strong chemisorption site in Co3ZnN/C as compared to that of Co4N. From the TPD results, the substitution of Co at A-site in Co4N using Zn could obviously increase the active sites for H2 chemisorption but weakens the interactions of atomic hydrogen with Co3ZnN/C surface [39].

Density functional theory (DFT) calculations are carried out to further confirm the origin of the excellent photoactivity of TMNs materials. The optimized structural representations of Co4N and Co3ZnN are presented in Fig. 5a-b. The band structure of the two samples calculated with Perdew-Burke-Ernzerhof (PBE) functional is shown in Fig. 5c-d, it reveals the metallic features of these two metal nitrides [40]. The valence bands of both samples have passed through Fermi level (zero) to enter their conduction bands, illustrating the existence of free electrons near the Fermi level, in good agreement with the density of states (DOS) plots, shown in Fig. 5e-f, indicating the metallic nature of both samples [41, 42]. Moreover, the electronic interaction, coupling the Co and N valence states with the Zn d-states in Co3ZnN, is clear from these plots. The PDOS contributed to the p orbitals of Nitrogen atoms are successive, suggesting a covalent
interaction among Co, Zn, and N in the energy region between -5 to -8 eV, far below the Fermi level. Unique cobalt and zinc bimetallic structure lead to covalent interaction. On the other hand, it has been reported repeatedly that the d-band center model can be considered as a good descriptor for the hydrogen and oxygen reactions of catalysts [43, 44]. The calculated d-band center of Co$_4$N and Co$_3$ZnN are -1.78 eV and -1.87 eV relative to the Fermi level, respectively. Therefore, the antibonding energy states are lowered and the d-band center of Co$_3$ZnN is more negative, far away from the Fermi level. These electronic changes might result in a weakened interaction between the material surface and hydrogen and meanwhile facilitates the desorption of hydrogen from the catalyst surface [17], which in parallel to the metal-like properties of this transition metal nitride could make the cornerstone of their excellent catalytic activity.

The possible mechanism of photocatalytic hydrogen evolution in the Eosin Y-sensitized Co$_3$ZnN/C nanocomposites in the TEOA aqueous solution system can be speculated like Fig. S14. Eosin Y (EY) is excited by the visible light and forms the singlet excited state (EY$_{1*}$). And then EY$_{1*}$ changed into the triplet excited state EY$_{3*}$ through fast intersystem crossing (ISC). In the presence of sacrificial donor TEOA, EY$_{3*}$ is then reductively quenched to EY$^-$[45]. The electrons of EY$^-$ species are stored by the carbon black with high electronic storage capacity and then transferred to Co$_3$ZnN nanoparticles on the surface of carbon black, while the EY$^-$ changing back to EY due to the loss of the electron. The electrons finally reduce H$_2$O to H$_2$ on the bimetallic active sites of Co$_3$ZnN nanoparticles.

3. Conclusions

In summary, an antiperovskite phase Co$_3$ZnN has been synthesized for efficient hydrogen evolution in the Eosin Y-sensitized system. The replacement of cobalt atom by zinc atom leads
to an improved charge transfer kinetics and catalytic properties compared with Co₄N. Carbon black support further reduces the particle size of Co₅ZnN and assists in the electron storage and adsorption capabilities. The optimal Co₅ZnN/C catalysts exhibit the H₂ evolution rate of 15.4 μmol mg⁻¹ h⁻¹, which is over 6 times higher than that of monometallic Co₄N. This work is expected to provide a new guideline for optimizing transition metal nitride to realize their efficient exploitation for solar energy conversion.

4. Experimental Section

4.1 Synthesis of Co₅ZnN/C nanocomposites

Different quality Co(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O (The molar ratio is 3:1) were dissolved in 100 mL ethanol to get the CoZn-precursor salt solution. 100 mg Carbon black were added into the CoZn-precursor salt solution and dispersed using ultrasound for 30 min. Then the liquid was dried under a constant temperature of 90 °C. The as-prepared precursor sample was left in a beaker and dried in a vacuum oven at 80 °C overnight. The dried CoZn/C precursor samples were transferred into a quartz boat after grinding and spread thinly on the boat. The samples were prepared in NH₃ flow (99.999%) of 100 sccm at 600 °C with a heating rate of 5 °C min⁻¹, and the maintained time is 1h. The black sample is the Co₅ZnN/C nanocomposites. The samples with different carbon content were prepared by controlling the mass ratio of carbon to the nitrate (Co₅ZnN/C (mass ratio 2:1), Co₅ZnN/C (mass ratio 1:1) and Co₅ZnN/C (mass ratio 1:2)). The schematic illustration is shown in Scheme S1. The reagents and the synthesis of the other contrast samples are shown in the Supplementary Information (SI).

4.2 Material characterization
The crystal structure for solid samples was characterized using an X-ray diffractometer (XRD, Rigaku Miniflex 600, Japan) in the 2θ range of 10-80° at a scan rate of 1° min⁻¹. Raman spectra were obtained on a confocal microprobe Raman system (Renishaw inVia Reflex). The diffuse reflectance spectra of the samples were measured in the range of 200-800 nm using a UV-vis spectrophotometer (UV-vis DRS, Hitachi U-3900, Japan) equipped with an integrating sphere attachment. Photoluminescence (PL) spectra of the different samples were investigated using a spectrophotometer (PL, Horiba Jobin Yvon Fluoromax 4C-L, France) with an excitation wavelength of 420 nm. To ensure the comparability of the PL spectra, the experimental parameters, including the excitation wavelength, slit width, and the amount of the samples, were identical. PL emission spectra of the catalysts- Eosin Y -TEOA suspensions at pH = 11 subjected to a 420 nm excitation. The concentration of Eosin Y and catalysts are 250 ppm and 0.0625 mg/mL, which are identical to the photocatalytic reaction condition. Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2010, USA) surface areas were determined at 77 K. Morphologies of the samples were characterized using a field-emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai F20 instrument. The H₂-TPD tests were carried out using a Micromeritics Autochem 2920 apparatus with a thermal conductivity detector (TCD). X-ray photoelectron spectroscopy (XPS) was performed using an AXIS Ultra DLD (Shimadzu, Japan) spectrometer with Al Kα excitation (1486.6 eV).

4.3 Photoactivity testing

Photocatalytic water splitting to H₂ was carried out in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. H₂ evolution analysis was performed by
dispersing 5 mg of catalyst powder and a certain quality of Eosin Y in 80 mL aqueous solution containing 8 mL TEOA (TEOA as the sacrificial electron donor). A 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfect Light Co., Ltd.) was applied as the light source, and visible light irradiation was realized by using a 400 nm cutoff filter. Continuous magnetic stirring was applied at the bottom of the reactor in order to keep the photocatalyst in suspension during the whole experiments. The temperature of the reaction solution was maintained at 278 K by a flow of cooling water during the reaction. The evolved H₂ was in situ monitored periodically using an online gas chromatograph with a thermal conductivity detector (FULI GC9790II, Ar as carrier gas). The details of the recycling test are shown in SI.

4.4 Electrochemical measurements and computational details

The electrochemical measurements and computational details are shown in SI.

Acknowledgment

This work is supported by the Natural Science Foundation of China (Grant No. 21471147 and 61971405). Minghui Yang would like to thank the Ningbo 3315 program and the Opened Fund of the State Key Laboratory on Integrated Optoelectronics (No. IOSKL2017KF08) for support. Siqi Liu would like to thank for the Natural Science Foundation of Zhejiang Province (LQ19B030001).

References


Captions of Figures

**Fig. 1** The Rietveld-fitted X-ray powder diffraction pattern of (a) Co$_3$ZnN and (b) Co$_4$N in ammonia at 600 °C. Charge density distribution of (200) surface in (c) Co$_3$ZnN and (d) Co$_4$N, respectively. More negative charge can be observed at N-Co-N network in Co$_3$ZnN than that in Co$_4$N.

**Fig. 2** TEM images and HRTEM images of (a,b) bulk Co$_3$ZnN and (c,d) Co$_3$ZnN/C(1:1) nanocomposites.

**Fig. 3** The XPS spectra of Co$_4$N, Co$_3$ZnN and Co$_3$ZnN/C(1:1) in the (a) Co 2p, (b) Zn 2p and (c) N1s regions. (d) The Raman spectrum of as-prepared catalysts.

**Fig. 4** (a) The average rates of H$_2$ evolution under visible-light (λ > 400 nm) over as-prepared Co$_4$N, Co$_3$ZnN and Co$_3$ZnN/C (1:1) samples in Eosin Y-TEOA system. (b) LSV curves of the as-prepared samples, the blank GCDE (electrode rotating speed, 1600 r.p.m.; scan rate, 100 mV s$^{-1}$). (c) Electrochemical impedance spectra of Co$_4$N, Co$_3$ZnN and Co$_3$ZnN/C(1:1) (AC voltage, -1.5 V; frequency range, from 10000 Hz to 0.1 Hz). (d) H$_2$-TPD profiles of Co$_4$N and Co$_3$ZnN/C(1:1) samples.

**Fig. 5** The atomic structure model of (a) Co$_4$N and (b) Co$_3$ZnN. The large pink and large gray balls show Co and Zn atoms respectively, and the O atom is shown by a small turquoise ball. The electronic structure of (c) Co$_4$N and (d) Co$_3$ZnN. Calculated electronic densities of states of (e) Co$_4$N and (f) Co$_3$ZnN. The Fermi level is set to zero.
Fig. 1 The Rietveld-fitted X-ray powder diffraction pattern of (a) Co₃ZnN and (b) Co₄N in ammonia at 600 °C. Charge density distribution of (200) surface in (c) Co₃ZnN and (d) Co₄N, respectively. More negative charge can be observed at N-Co-N network in Co₃ZnN than that in Co₄N.
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**Fig. 4** (a) The average rates of H\textsubscript{2} evolution under visible-light (\(\lambda > 400\) nm) over as-prepared Co\textsubscript{4}N, Co\textsubscript{3}ZnN and Co\textsubscript{3}ZnN/C (1:1) samples in Eosin Y-TEOA system. (b) LSV curves of the as-prepared samples, the blank GCDE (electrode rotating speed, 1600 r.p.m.; scan rate, 100 mV s\textsuperscript{-1}). (c) Electrochemical impedance spectra of Co\textsubscript{4}N, Co\textsubscript{3}ZnN and Co\textsubscript{3}ZnN/C(1:1) (AC voltage, -1.5 V; frequency range, from 10000 Hz to 0.1 Hz). (d) H\textsubscript{2}-TPD profiles of Co\textsubscript{4}N and Co\textsubscript{3}ZnN/C(1:1) samples.
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